

Comparative Study between Natural and Artificial Zeolites as Supports for Biosorption Systems

Maria Teresa Tavares^{1a}, Cristina Quintelas^{1b}, Hugo Figueiredo^{1c}, Isabel Neves^{2d}

¹Centro de Engenharia Biológica, Universidade do Minho, Campus de Gualtar, 4710-057 Braga, Portugal

²Departamento de Química, Universidade do Minho, Campus de Gualtar, 4710-057 Braga, Portugal

^attavares@deb.uminho.pt; ^dineves@quimica.uminho.pt

Keywords: Natural zeolites; Biosorption; Biofilm; Chromium; NaY; NaX

Abstract. This study aims the definition of a new material that may act as a robust and yet cost effective biosorbent for treatment of wastewater with low concentration of heavy metals. A comparative study was made between two biosorption systems composed of an *Arthrobacter viscosus* biofilm supported on Cuban natural zeolites and on prepared NaY and NaX, in terms of their ability to retain ionic chromium. The bacterium is able to reduce Cr(VI) to Cr(III) and, only then, this smaller and positive ion may be entrapped in the zeolite cages by ion exchange. The first support was tested in a continuous flow semi-packed bed column. The highest removal ratio, 42%, was achieved for initial chromium concentration of 10 mg/L, but the best up-take, 5.5 mg/g_{zeolite}, was obtained for initial concentration of 70 mg/L. Biosorbents prepared with the same biofilm supported in NaY and NaX zeolites were also considered in batch studies, with a typical kinetics of biosorption processes, reaching 20% of initial chromium removal within an initial range of Cr(VI) concentration between 50 and 250 mg/L. These last structures were characterized by spectroscopic methods (FTIR and ICP-AES), surface analysis (DRX) and thermal analysis (TGA). All these techniques indicated that the biosorption process does not modify the morphology and structure of the FAU-zeolites.

Introduction

Heavy metals like cadmium, chromium and lead are priority pollutants and industrial wastewater with low concentrations of these elements is still an environmental problem, as classical treatment processes like chemical precipitation, coagulation or membrane separation are quite expensive mainly for small and medium size industries operating with tight budgets. Alternative processes are needed and biosorption performed by an adequately supported biofilm may become quite attractive in terms of initial investment and maintenance costs. Biosorption is the accumulation of metals by biological materials without active uptake and can be considered as a collective term for a number of passive accumulation steps which may include ion exchange, coordination, complexation, chelation, adsorption and microprecipitation [1]. Bacteria are quite adequate for heavy metals biosorption due to their ability to sorb metal ions, suitability for natural environments and low cost [2]. Among many, *Arthrobacter viscosus* appears as a good exopolysaccharide producer, which, by itself, would allow foreseeing good qualities for support adhesion and metal ions entrapment [3]. Zeolites are hydrated aluminosilicate minerals with a cage-like structure that offers large internal and external surface areas for ion exchange. These cages are filled with ions and water molecules with high freedom of movement. They possess a net negative structural charge due to isomorphic substitution of cations in the mineral lattice. Hence they have a strong affinity for transition metal cations, but only little affinity for anions and non-polar organic molecules [4]. This may be changed by surface pre-treatment or surface coverage by a specific biofilm. Zeolites are quite common and

naturally occurring zeolites from Cuba were tested in this study. They are mainly composed of clinoptilolite (80%), one of the most efficient materials in terms of heavy metals fixation [5]. For comparison purposes the same biofilm was supported on NaX and NaY and the resulting material was evaluated in terms of retention efficiency and final properties.

Materials and Methods

The bacterium *Arthrobacter viscosus* was obtained from the Spanish Type Culture Collection of the University of Valência. Aqueous chromium solutions were prepared by diluting $K_2Cr_2O_7$ in distilled water. All glassware used for experimental purposes was washed in 60% nitric acid and subsequently rinsed with deionised water to remove any possible interference by other metals. Atomic absorption spectrometric standards were prepared from $1000\text{ mg}_{Cr}\text{ l}^{-1}$ solution.

The supports were naturally occurring zeolite from Cuba, mainly composed by clinoptilolite, $Al_2O_3 \cdot SiO_2$, with a pore diameter between 0.2 and 1.2 nm and a internal surface smaller than $10^3\text{ m}^2\cdot\text{g}^{-1}$. This material was randomly smashed and only particles with a size between 2 and 5mm were used.

The whole experimental work was conducted in duplicate. The Cuban zeolite was placed in Erlenmeyer flasks of 250 ml with 150 ml of distilled water. It was sterilised at 120°C for 20 min to release the air inside the pores. Then, this material was placed in mini-columns (internal diameter = 0.9 cm, ht = 30 cm) for continuous flow system studies. The microorganism culture and the nutrient broth were pumped through at a flow rate of 25 ml/min, aiming the formation of the biofilm. The high flow rate used allows the formation of a compact biofilm and consequently a resistant one to the erosion stress resultant from the hydrodynamic forces.

After the biofilm formation, the bed was washed out and the metal solution with concentrations between 10 and 150 mg/l, with pH ranging from 4.5 to 5.5 and a temperature of 26°C , was passed through the columns with a flow rate of 10 ml/min. At the end of each run, columns were washed out and samples of the effluent were seeded in Petri plates with nutrient agar to assess the metabolic activity of the microorganism. Cr (VI) concentration at the inlet and at the outlet of the sequential columns was measured by Atomic Absorption Spectroscopy, Varian Spectra AA-250 Plus, by acetylene flame emission and wavelengths of 357.9 nm, 425.4 nm and 520.8 nm.

The faujasite zeolites NaY (Si/Al = 2.88) and NaX (Si/Al = 1.63) were obtained from W.R. Grace. The zeolites were calcinated at 500°C during 8 hours under a dry air stream prior to use. The biofilm formation was carried out in batch units and all experimental work was conducted in triplicate. Batch adsorption experiments were conducted using 1.0 g of the Y or X zeolites with 150 mL of the different dichromate solutions (50, 100, 150 and 250 mg_{Cr}/L) and 15 mL of *Arthrobacter viscosus* culture media in a 250 mL Erlenmeyer flask. For the microorganism growth a medium with 5 g/L of peptone, 3 g/L of malt extract, 3g/L of yeast extract and 10 g/L of glucose was used, sterilized at 120°C for 20 min. The Erlenmeyer flasks were kept at 28°C , with moderate stirring. Samples (1 mL) were taken, centrifuged and analyzed for metals using atomic absorption spectrophotometry (AAS), using a Varian Spectra AA-400. Room temperature FTIR spectra of the samples were recorded on a Bomem MB104 spectrometer. The transmission spectra of the powdered samples were obtained using KBr pellets over the range $4000\text{--}600\text{ cm}^{-1}$ by averaging 20 scans at a maximum resolution of 4 cm^{-1} . X-ray diffraction patterns were recorded using a Philips Analytical X-Ray model PW1710 BASED diffractometer system. The solids samples were exposed to the Cu $K\alpha$ radiation at room temperature in a 2θ range between 5 and 70° . Thermogravimetric analyses of samples were carried out using TGA 50 Shimadzu instrument under high purity helium supplied at a constant 50 mL min^{-1} flow rate. All samples were subjected to a 6°C min^{-1} heating rate and were characterized between 25 and 600°C . The elemental chemical analyses (Si, Al, Na and Cr) were performed by University of Minho, Departamento de Ciências da Terra, using inductively coupled plasma atomic emission spectroscopy (ICP-AES).

Results and Discussion

In all the experiments the removal of Cr(VI) was very fast and presented a typical biosorption kinetics, which includes two phases: the first one is associated with the external cell surface, biosorption itself, and the second one is an intra-cellular accumulation/reaction, depending on the cellular metabolism [6].

The applicability of such retention system on practical situations depends on many factors, one of which is the initial concentration of metal on the liquid solution. As this process is to be applied to diluted solutions, the tested range of initial concentrations was defined bellow 100 mg/L. Figure 1 shows the dependence of the total uptake of the metallic ion as a function of the initial concentration on the water solution. There is a clear maximum around 70 mg/L and this value established the initial conditions of the future experiments. This maximum is probably defined by the balance between the effect of the increasing driving force in terms of concentration difference between the bulk solution and the biosorbent surface and the effect of the saturation of the surface matrix.

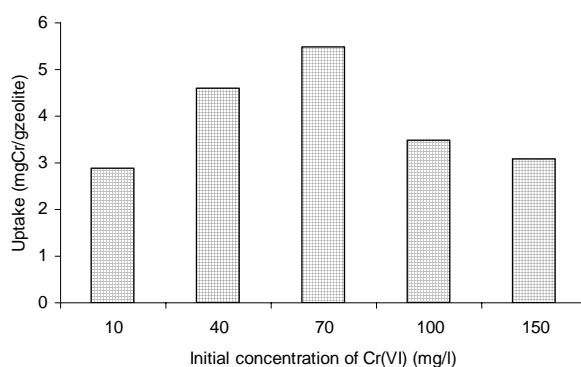


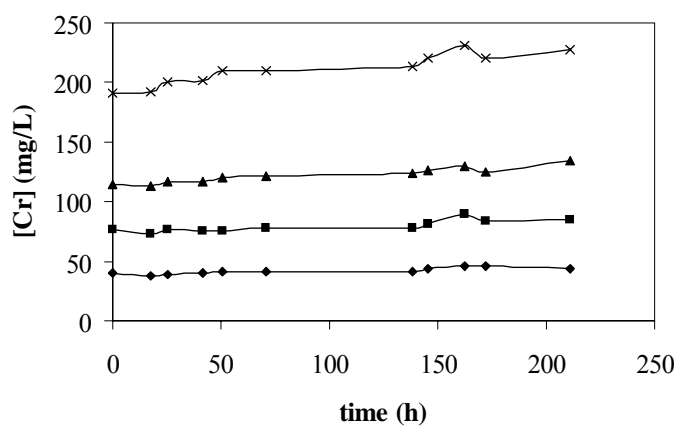
Figure 1. Uptake of Cr (VI) by a biofilm of *Arthrobacter viscosus* supported on natural zeolite as a function of the initial concentration of the metal in the water solution to be treated.

Several studies show that the modifications on the surface of zeolites give them positive charge, can increase the efficiency of the system to remove chromium. Batista [7] prepared an organo-zeolite by modification of the surface adsorptive properties of natural zeolites (clinoptilolite) from Cuba, with a cationic surfactant, Br-HDTMA, and obtain an adsorbent with a maximum removal capability of Cr (VI) of 30 mg/g_{organo-zeolite}, without biosorption. Barros [8] justified the low efficiency of natural zeolites on the removal of chromium with the presence of impurities, the difference between the relative big anionic radius of chromium and the porous diameter of the zeolite and the strong tendency of chromium to form complexes.

The experimental data of adsorption of chromium by a biofilm of *Arthrobacter viscosus* supported on NaY and NaX zeolites varying the metal concentration from 50 to 250 mg_{Cr}/L are present in Figure 2. In steady-state conditions no difference between the two supports is detected and the same is observed at higher initial concentrations. The maximum removal efficiency was 20% for chromium in both systems, achieved during the initial seconds of the experiment [10].

The relatively low maximum removal efficiency seems to be connected with the lack of affinity between the anionic charge of CrO_4^{2-} and the anionic charge of the bacteria and with the high ionic radius of the chromium ion. Although, zeolites have high surfaces areas (500-700 m²g⁻¹), most of this area is internal. These limitations probably reduce the adhesion of the *Arthrobacter viscosus* bacterium on the support.

a)



b)

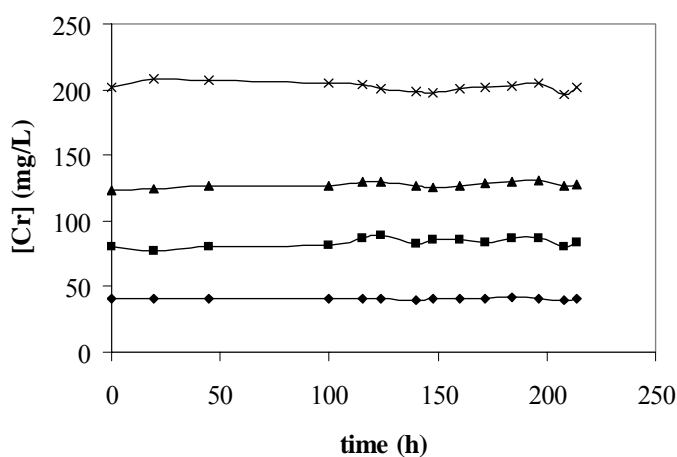


Fig. 2. Removal of chromium by a biofilm of *Arthrobacter viscosus* supported on (a) Y and (b) X zeolites for different chromium concentration: (x) 250 mg_{Cr}/L, (▲) 150 mg_{Cr}/L, (■) 100 mg_{Cr}/L and (◆) 50 mg_{Cr}/L.

Conclusions

The highest removal ratio, 42%, was achieved by a biofilm supported on natural zeolite for initial chromium concentration of 10 mg/L, but the best up-take, 5.5 mg/g_{zeolite}, was obtained for initial concentration of 70 mg/L.

A biofilm of *Arthrobacter viscosus* supported on Y and X zeolites is able to remove chromium from dilute solutions and can be applied in wastewater remediation. The reduction of Cr(VI) to Cr(III) is performed by the biofilm itself. This metal is exchanged in the zeolite without damage to the original matrix or loss of its crystallinity.

Aknowledgements

The authors would like to thank Dr. A. S. Azevedo for collecting the powder diffraction data and Dr. C. Ribeiro, from de Departamento de Ciências da Terra da Universidade do Minho, for chemical analysis and Dr. Gerardo Rodríguez, from La Habana University, for kindly yielding the clinoptilolite. They also acknowledge the material support of this project by the Fundação para a Ciência e Tecnologia, Ministério da Ciência e Tecnologia, Portugal (POCTI/EQU/12017/2001 and POCTI/QUI/44840/2002), financed by FEDER.

References

- [1] J.R. Duncan, D. Brady and A. Stoll, Environ. Technol. No. 15 (1994) 429
- [2] A. Scott and S.J. Palmer, Cadmium bio-sorption by bacterial exopolysaccharide. *Biotechnol. Lett*, 1988, **10**: 21-24.
- [3] C. Quintelas and T. Tavares, Removal of chromium(VI) and cadmium(II) from aqueous solution by a bacterial biofilm supported on granular activated carbon, *Biotechnol. Letters*, Vol. 23 (2001) 1349.
- [4] M.V. Mier, R.G. Callegas, R. Gear, B.E.J. Cisneros and P.J.J. Alvares, Heavy metal removal with Mexican clinoptilolite: multi-component ionic exchange. *Wat. Res.*, 2001, **25**: 373-378.
- [5] R. Arriagada, R. Garcia and R. Cid, Retention of chromium and mercury with natural and synthetic zeolites. In *Catalizadores y adsorbentes para la protección ambiental en la región Iberoamericana*, Ed. J. Blanco, P. Avila, CYTED, Madrid, 2001, pp 207-211.
- [6] M.T. Tavares, C. Martins and P. Neto, Biotreatment of Cr (VI) Effluents. In *Hazardous and Industrial Wastes*, Sengupta, AK, ed., Lancaster: Tecnomics Publishing Co., 1995, pp. 223-232.
- [7] M. Batista, M. Laza, G.R. Fuentes and J.L. Ruiz, Preparation and characterisation of a natural zeolites modified with the cationic surfactant BR-HDTMA, for Cr (VI) removal, *Jornadas Iberoamericanas de Catálisis Ambiental*, pp 294, Universidad Internacional de Andalucía, 2000.
- [8] M.A. Barros, N. Machado, E. Sousa-Aguiar, F. Alves and S. Pedroza, Removal of Cr³⁺ from industrial and synthetic wastewater by naturally occurring clinoptilolite. In *Catalizadores y adsorbentes para la protección ambiental en la región Iberoamericana*, Ed. J. Blanco, P. Avila, CYTED, Madrid, 2001, pp 219-224.